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Formation of gold-coated multilayer graphene via thermal reduction

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ABSTRACT

The gold-coated multilayer graphene was obtained by simultaneous thermal reduction of gold ions and graphene oxide blend film under argon flow for an hour. The effects of thermal reduction temperatures (200 °C, 400 °C, and 500 °C) on the structural, optical, and electrical properties of gold-coated multilayer graphene were studied by using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), UV–vis spectroscopy, and four point probe measurement. The optical transmittance increased and the sheet resistance decreased with the thermal reduction temperature. The highest optical transmission of 66% and the lowest sheet resistance of 78.3 kΩ/sq were obtained at thermal reduction temperature of 500 °C.

1. Introduction

Indium tin oxide (ITO) and fluorine-doped tin oxide (FTO), with good transparency and high conductivity at room temperature [1], have been widely used as transparent electrode in solar cell application [2–5]. Recently, the research interest has focused on graphene which can serve as alternative transparent electrode due to its high electrical conductivity [2,3], high optical transmission [6], chemical stability, low cost [7], and availabilty [8,9]. However, efforts to further improve its properties through simple, cheaper, and environmental friendly methods still remain a great challenge to researchers.

Multilayer graphene (MLG) has been obtained through thermal reduction of graphene oxide (GrO) film prepared by chemical route using the modified Hummers method in previous work [9]. However, the properties of resultant MLG are strongly dependent on the synthesis protocol [10]. The presence of functional groups during graphite oxide (GO) flake preparation could change the electronic-structure [11] and high energy induced by ultrasonic agitation during GrO preparation could damage its lattice-structure [12]. Besides, point defects and wrinkles could be formed during GrO thermal reduction [13]. All those factors contribute to lower optical transmittance and higher sheet resistance.

Kim et al. reported that spin coating of gold(III) chloride ($AuCl_3$) solution on graphene film leads to 77% decrease in sheet resistance and only 2% decrease in optical transmittance [14]. The decrease in sheet resistance is due to p-doping of graphene by reduction of gold ion to gold particle. However, the reduction of sheet resistance in multilayer graphene layer is not significant as compared to that in single or two layers graphene. Meanwhile, Le et al. demonstrated that gold nanoparticles-coated graphene could be obtained by adding gold(III) chloride hydrate ($HAuCl_4$) to the GrO aqueous solution followed by chemical reduction of GrO and gold ion by using polyelectrolyte (PDDA) as reducing agent and stabilizer [15].

It is well known that gold chloride tetrahydrate ($HAuCl_4 \cdot 3H_2O$) could be decomposed to gold particle when heated at and above 200 °C [16]. In addition, thermal reduction is also considered as one of most famous techniques to produce graphene from graphene oxide film [17]. In this work, a simple approach to simultaneously reduce the graphene oxide and gold ion by applying heat treatment at different temperatures was explored. The X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) results confirm that graphene oxide and gold ion have been successfully reduced and gold-coated multilayer graphene (Au-MLG) was obtained. The optical transmittance of Au-MLG increased whereas the sheet resistance decreased with the thermal reduction temperature.

2. Experimental

GO flake was prepared by using the modified Hummers method and the synthesis details were described elsewhere [9]. The typical gold-coated graphene oxide (Au-GrO) films preparation step is shown below: GO flake was dissolved in 0.01 M

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aqueous solution of $HAuCl_4 \cdot 3H_2O$ (99.999%, Sigma-Aldrich) at a concentration of 10 mg ml^{-1}. The solution underwent sonication for 30 min and followed by stirring for an hour. Then, the solution was spin-coated on quartz substrates to obtain Au-GrO films by using Chemat Technology KW-4A spin-coater. The Au-GrO films were then annealed at 200 °C, 400 °C, and 500 °C in argon atmosphere for an hour to form Au-MLG. The resultant samples were then denoted as Au-MLG2, Au-MLG4, Au-MLG5 for thermal reduction temperatures of 200 °C, 400 °C, and 500 °C, respectively.

The optical transmission characterization of Au-GrO and Au-MLG films was carried out by using Halo DB-20 UV–vis spectrophotometer. The crystal-structure was characterized by using Bruker D8 Advanced X-ray diffractometer with CuKα radiation at a scan rate of 0.025°/0.1 s. The morphology of the samples was obtained by using Zeiss Supra 55VP field emission scanning electron microscope (FESEM) at an acceleration voltage of 3 kV. Lastly, the sheet resistance was obtained via four point probe measurement using Keithley 2401 source meter.

3. Results and discussion

The XRD spectra of Au-GrO and Au-MLG films are shown in Fig. 1. A sharp peak at $2\theta = 9.82°$ corresponding to interlayer distance of C–C of 0.90 nm was observed in the XRD spectrum of Au-GrO. A weaker peak at $2\theta = 20.55°$ shows the incomplete oxidation and intercalaction of graphite [9]. It is interesting to note that another two peaks at $2\theta = 38.19°$ and 44.40° associated with (111) and (200) planes of anatase phase of gold, respectively can be identified (JCPDS file no. 00-004-0784). This indicates that some of the Au^{3+} ions could be reduced to Au^0 particles without any thermal treatment. It has been reported that Au^{3+} ions could be easily reduced on the graphene to form Au^0 particles as described by the following reaction [14]:

$$AuCl_4^{-} + 3e \rightarrow Au^0 + 4Cl \qquad (1)$$

This reduction process is possible since the oxidation of graphite is incomplete in present work. In addition, some Au^0 particles could also be produced on sonication via the following reactions [18]:

$$H_2O \rightarrow H^* + {}^*OH \qquad (2)$$

$$AuCl_4^{-} + 3H^* \rightarrow Au^0 + 4Cl^{-} + 3H^{+} \qquad (3)$$

After thermal reduction at 200 °C, the sharp peak at $2\theta = 9.82°$ disappeared and a broad peak at $2\theta = 22.05°$ corresponding to the interlayer distance of C–C of 0.404 nm was detected, suggesting removal of functional groups such as hydroxyl (OH), epoxy (C–O–C) and carboxyl (COOH) from Au-GrO film [9,15,19,20]. The interlayer distance of C–C decreased further to 0.396 nm ($2\theta = 22.90°$) and 0.394 nm ($2\theta = 23.05°$), at temperatures of 400 °C and 500 °C, respectively, indicating more functional groups could be removed at higher temperature. Two peaks corresponding to (111) and (200) planes of gold became more pronounced at temperatures of 200 °C and 400 °C. This is due to the thermal decomposition of $HAuCl_4 \cdot 3H_2O$ to Au when the heating temperature reached 200 °C according to the following reaction [16]:

$$HAuCl_4 3H_2O \overset{100^\circ C}{\Longrightarrow} AuCl_3 \overset{160^\circ C}{\Longrightarrow} AuCl \overset{200^\circ C}{\Longrightarrow} Au \qquad (4)$$

Since Au-MLG heated at 500 °C had the smallest number of remaining functional groups, gold ions were reduced more uniformly on the graphene. As a result, well distributed and smaller size of gold was formed as evidenced by the broadened XRD peak of gold plane.

Fig. 2 shows the optical transmission spectra of Au-GrO, Au-MLG2, Au-MLG4, and Au-MLG5 films. The transmittance of Au-GrO film reduced significantly from 75% ($\lambda = 550$ nm) to 53% when the film was heated at 200 °C as a result of partial restoration of conjugated C=C bonds in the graphene structure [21]. In contrast to pristine graphene, increasing the thermal reduction temperature did not lead to decrease in optical transmittance, but to an increment. A valley at around 650 nm in the optical transmission spectra of Au-MLG2 and Au-MLG4 films could be related to plasmonic band of aggregative states of gold nanoparticles [22]. On the other hand, a valley at around 550 nm corresponding to plasmonic band of ordinary gold nanoparticles was observed in the optical transmission spectra of Au-MLG5 film. This suggests that the gold particles tended to aggregate together at lower thermal reduction temperature. A more complete decomposition of $AuCl_3$ and reduction of gold aggregations lead to increase in transmittance with thermal reduction temperature due to lesser scattering effect.

Fig. 3 shows the typical FESEM images of Au-MLG films prepared at thermal reduction temperature of 400 °C and 500 °C. The particle size of gold on Au-MLG4 film was larger than that on Au-MLG5 film, providing further evidence for the formation of gold aggregate at lower thermal reduction temperature. The Au-MLG5 film was also flatter than the Au-MLG4 film probably due to inhibition of wrinkle formation by Au nanoparticles. In addition, it can be seen that more Au particles were formed on the wrinkles, which is well in line with other report [14].

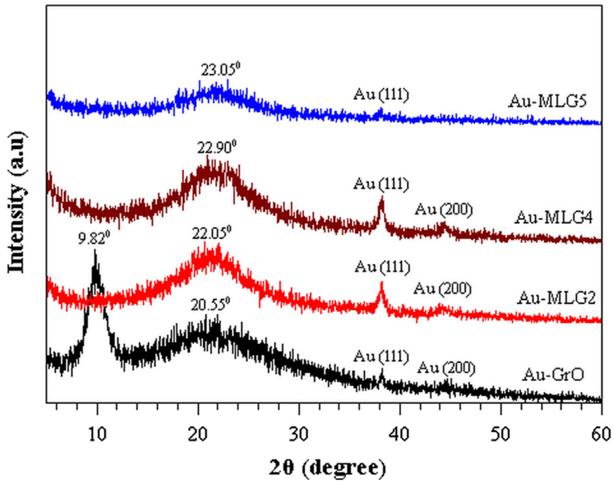

Fig. 1. The XRD spectra of Au-GrO, Au-MLG2, Au-MLG4, and Au-MLG5 films.

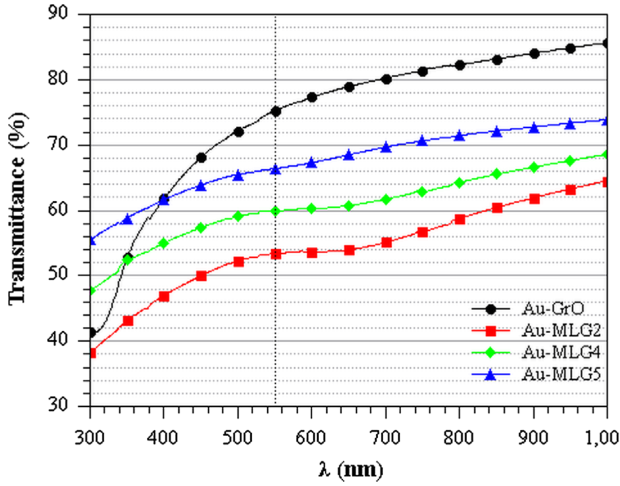

Fig. 2. The optical transmission spectra of Au-GrO, Au-MLG2, Au-MLG4, and Au-MLG5 films.

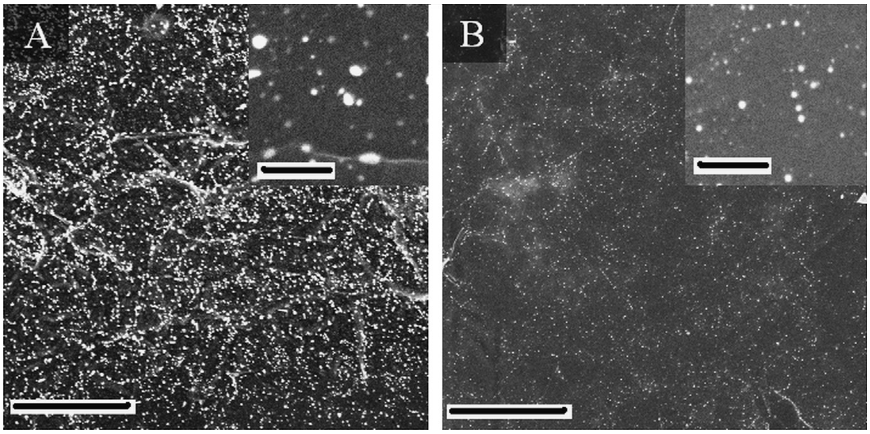

Fig. 3. FESEM images of (A) Au-MLG4 and, (B) Au-MLG5 (scale bar=2 μm). The insets show the respective enlarged FESEM images (scale bar=200 nm).

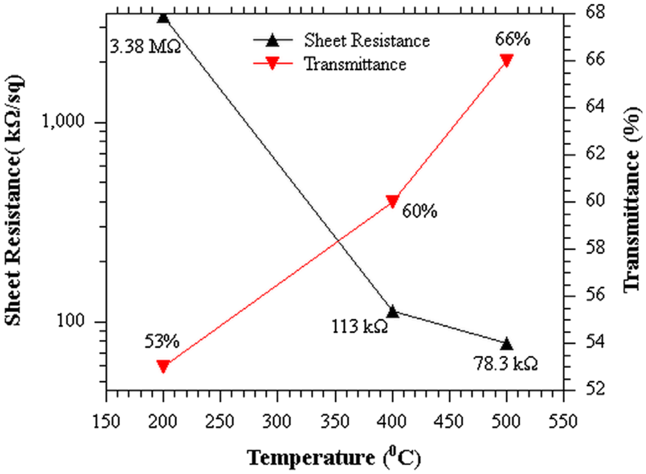

Fig. 4. The sheet resistance and optical transmittance ($\lambda = 550$ nm) of Au-MLG films as a function of thermal reduction temperature.

Fig. 4 shows the sheet resistance and optical transmittance ($\lambda = 550$ nm) of the Au-MLG films prepared at different thermal reduction temperatures. The optical transmittance increased whereas the sheet resistance decreased as the thermal reduction temperature increased. The optimum optical transmittance of 66% and sheet resistance of 78.3 kΩ/sq were achieved at thermal reduction temperature of 500 °C. The decrease in sheet resistance is mainly attributed to restoration of larger portion of conjugated C=C bonds in the graphene structure at higher temperature [21]. It is also worth noting that the sheet resistance of Au-MLG heated at 500 °C was slightly smaller than that of MLG (91.6 kΩ/sq) heated at the same temperature (Ali Umar, MI, unpublished data). It is believed that p-doping of graphene by gold ions [14] and creation of direct conductive path between graphene sheets connected by the gold particles [23] contribute to the reduction in sheet resistance.

4. Conclusions

The effects of thermal reduction temperature on the structural, optical, and electrical properties of Au-MLG films have been investigated. The graphene oxide and gold ions have been successfully reduced to form Au-MLG film at and above 200 °C. The optical transmittance of Au-MLG films increased with the thermal reduction temperature as a consequence of more complete decomposition of $AuCl_3$ and reduction of gold aggregations. Meanwhile, the reduction in sheet resistance with thermal reduction temperature is mainly ascribed to restoration of conjugated C=C bonds in the graphene structure. The highest optical transmittance of 66% and the lowest sheet resistance of 78.3 kΩ/sq were obtained at thermal reduction temperature of 500 °C.

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